

Simultaneous spectrophotometric determination of heavy metal ions Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with Br-PADAP in primary reactor coolant system

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1. Introduction

The performance with integrity of nuclear power plants is highly influenced by the presence of the corrosion products. The deposition of corrosion products in the steam generator is the one of the main concerns of power plants. Of course, the amount of deposited corrosion product in the steam generator is highly dependent on the corrosion products in the cooling water. In addition, the activated corrosion products are also a management object to reduce the level of radiation exposure to power plant operators. Therefore, the quantification of corrosion products is considered of importance.

In this study, we applied the spectrophotometric method to detect metal ions such as iron, cobalt, nickel, copper, and zinc, which are major elements of structural material of the plant. In particular, the chemical complexation of those divalent metal ions with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) provides high molar absorptivity [1]. For the simultaneous determination of metal ions, a partial least square (PLS) regression method was applied.

2. Experimental

0.1 M stock solutions of metal ions (iron, cobalt, nickel, copper, and zinc) were prepared by dissolution of their chloride form in 1 M HCl and 1 M NH₂OH·HCl. The purity of metal chlorides are over 99.99%. 0.2 M sodium acetate/acetic acid, imidazole/HCl, and Tris/HCl were prepared to control the pH of the solution. A 10⁻³ M stock solution of Br-PADAP was prepared dissolved in ethanol. All aqueous solutions were prepared by using deionized water from a Milli-Q system. A 10⁻⁵ M of Br-PADAP was prepared in aqueous 50 % (v/v) ethanol solution with concentration of 0.01 M pH buffer. Metal ion solutions were added just before the measurement.

All absorption spectra were determined with an UV-Vis absorption spectrometer (Carl-Zeiss, MCS 601 UV-NIR C) with halogen lamp using 1.0 cm quartz cuvette and 100 cm liquid waveguide capillary cell (LWCC).

3. Results

Metal ions mentioned above form 1:2 complex with Br-PADAP, except for copper, which forms 1:1 complex, have high molar extinction coefficients (>

4×10⁴ M⁻¹cm⁻¹). Although Br-PADAP is soluble in ethanol/water mixture, 10⁻⁵ M Br-PADAP was not stable in mixture lower than 50 % (v/v) of ethanol concentration. Surfactants such as Triton X-100 increased the solubility and the stability of the Br-PADAP and its complex, but retarded the reaction rates. Thus, all absorption spectra of the complex were measured in aqueous 50 % (v/v) ethanol solution without Triton X-100.

Figure 1 shows the absorption spectra of iron, cobalt, nickel, copper, and zinc. The concentration of metal ions and Br-PADAP were 10⁻⁴ mol/L and 10⁻⁵ mol/L, respectively. The absorption spectra of the complex showed clear double maxima located between 500 ~ 600 nm. For iron, an absorption band was seen at 750 nm, which optical characteristics can be distinguished from others. The absorption maxima of each metal complex are shown in Table.1 Detection limits of metal ions were less than 1 ppb with 1.0 cm cuvette. With 100 cm LWCC, the detection limit of tens of ppt concentration range can be also achieved.

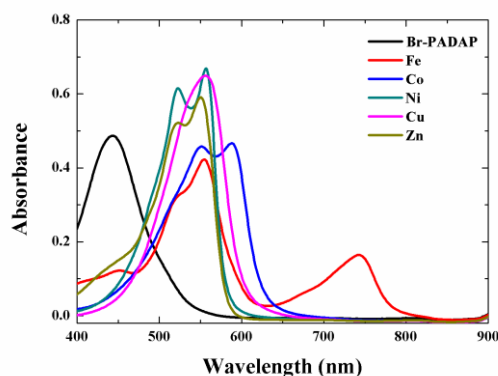


Figure 1. Absorption spectra of Br-PADAP both before and after complex formation with metal ions ([Br-PADAP]=10⁻⁵ M, [Me]=10⁻⁴ M, [EtOH]=50% (v/v), pH=7)

Table 1. Molar extinction coefficients for metal ions

Metal ion	Molar extinction coefficient (10 ⁴ M ⁻¹ cm ⁻¹)
Iron	4.2
Cobalt	4.7
Nickel	6.7
Copper	6.5
Zinc	5.9

Copper and zinc formed complexes immediately after the reaction and reached its maximum absorbance value, which was stable for at least 24 hours. In case for iron, its maximum absorbance was reached within 30 seconds, however, for cobalt and nickel, it took 15 minutes to reach maximum absorbance.

Figure 2 shows the change in absorption spectra according to reaction time for cobalt and nickel. As seen in the figure, cobalt and nickel have different absorbance patterns. In case for cobalt, the first absorption band (550 nm) was seen immediately as soon as the reaction was started, but for the latter one (588 nm), a gradual increase can be seen with reaction time. However, for the case of nickel, both the absorption bands at 523 nm and 556 nm increased gradually and the ratio between the two absorption bands remained constant. This phenomena may be due to the different formation mechanism of the complexes and further study is now on-going to prove the formation mechanism.

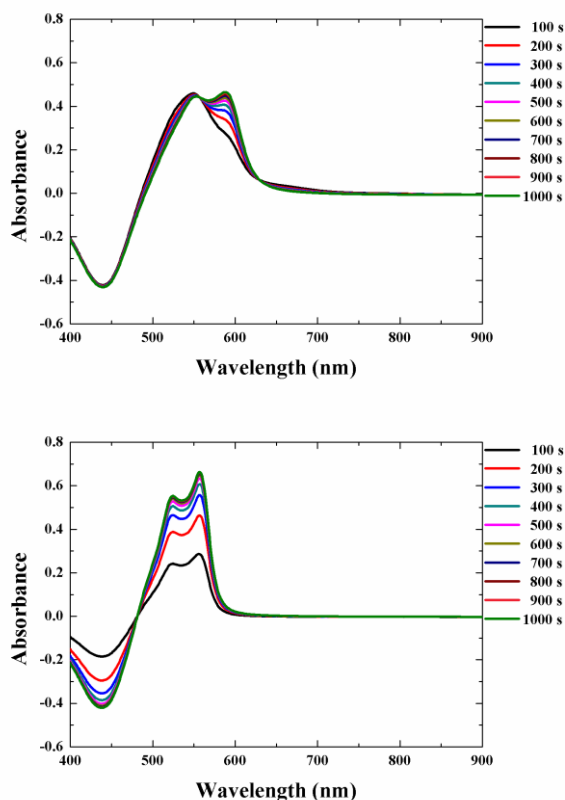


Figure 2. Absorption spectra of Br-PADAP complex of cobalt (top) and nickel (bottom) with varying reaction time ($[Br-PADAP]=10^{-5}$ M, $[Me]=10^{-4}$ M, $[EtOH]=50\%$ (v/v), $pH=7$)

The PLS regression method by using MATAB code [2] was applied for the simultaneous spectrophotometric determination of metal ions. The difficulty imposed by overlap of the absorption spectra was overcome by the PLS regression method. The average of relative errors

was less than 5 % and the relative errors were no greater than 7% in most cases.

4. Conclusions

In the present work, the complexation of Br-PADAP with divalent metal ions (iron, cobalt, nickel, copper and zinc) was studied. The PLS regression method was successfully applied for simultaneous elemental detection in multi-element systems. These results suggests that the method is very ample to detect corrosion products in nuclear power plants.

REFERENCES

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